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(54) Fuel compositions with enhanced combustion characteristics.

(57) Fuels, methods of producing fuels, and methods of using fuels to reduce the amount of atomospheric pollutants (NOx, CO, and/or hydrocarbons) formed on combustion of middle distillate fuels in engines or burner apparatus. These results can be achieved without concomitant increases in emissions of particulates. The fuels contain less than 500 ppm of sulfur and at least one organic nitrate combustion improver.

EP 0 457 589 A1

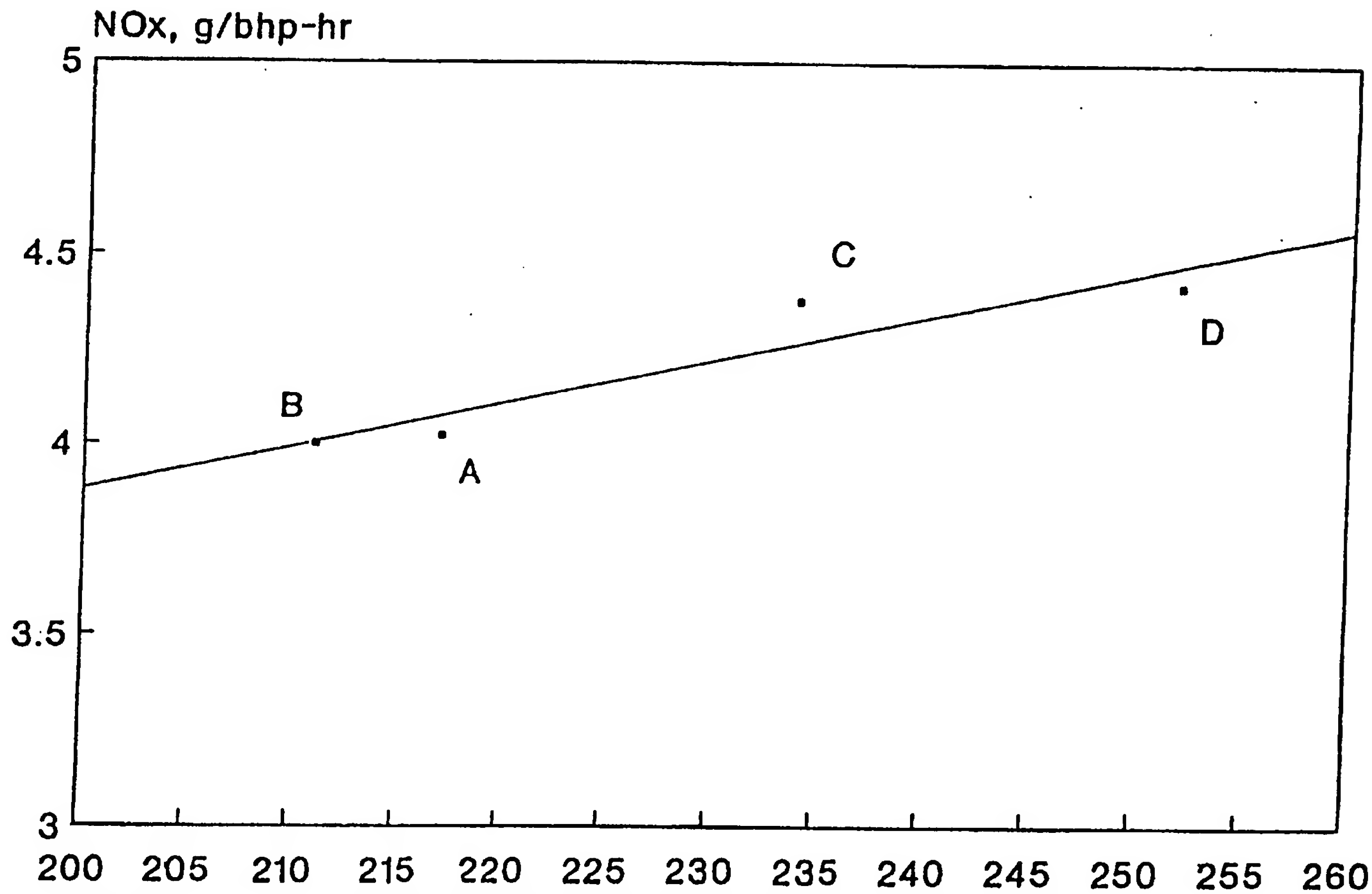
NOx, g/bhp-hr
5
4.5
4
3.5
3
B
A
C
D
200
205
210
215
220
225
230
235
240
245
250
255
260
10% boiling temperature, deg. C

FIG. 1

This invention relates to preservation of the environment. Mor particularly, this invention relates t fuel compositi ns and methods that reduce atmosph ric pollution normally caused by the operati n of engines r combustion apparatus on middle distillate fuels.

The importance and desirability of reducing the release of pollutants into the atmosphere are well recognized. Among the pollutants sought to be reduced are nitrogen oxides ("NO_x"), carbon monoxide, unburned hydrocarbons, and particulates.

This invention involves the discovery, inter alia, that it is possible to reduce the amount of NO_x or CO or unburned hydrocarbons released into the atmosphere during operation of engines or other combustion apparatus operated on middle distillate fuel by employing as the fuel a middle distillate fuel having a sulfur content of 500 ppm or less and having dissolved therein a combustion improving amount of at least one organic nitrate combustion improver. In fact it has been found possible through use of such fuel compositions to reduce the amount of two and in some cases all three such pollutants (NO_x, CO and unburned hydrocarbons) emitted by diesel engines. Moreover this important and highly desirable objective has been and thus may be achieved without suffering an undesirable increase in the emission of particulates. This is a unique discovery since the available experimental evidence and mechanistic theories of combustion suggest that if NO_x is reduced, the amount of particulates will be increased, and vice versa.

Accordingly this invention provides in one of its embodiments a fuel composition characterized in that it comprises a major proportion of a hydrocarbonaceous middle distillate fuel which has a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and in that said fuel contains a minor combustion-improving amount of at least one organic nitrate combustion improver dissolved therein. By the term "hydrocarbonaceous" as used in the ensuing description and appended claims is meant the middle distillate fuel is composed principally or entirely of fuels derived from petroleum by any of the usual processing operations. The finished fuels may contain, in addition, minor amounts of non-hydrocarbonaceous fuels or blending components such as alcohols, dialkyl ethers, or like materials, and/or minor amounts of suitably desulfurized auxiliary liquid fuels of appropriate boiling ranges (i.e., between about 160 and about 370°C) derived from tar sands, shale oil or coal. When using blends composed of such desulfurized auxiliary liquid fuels and hydrocarbonaceous middle distillate fuels, the sulfur content of the total blend must be kept below 500 ppm.

In another of its embodiments this invention provides improvements in combustion processes wherein a hydrocarbonaceous middle distillate fuel is subjected to combustion in the presence of air. Such improvement comprises providing as a fuel used in such process a hydrocarbonaceous middle distillate fuel having a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and having dissolved therein a minor combustion improving amount of at least one organic nitrate combustion improver.

Still another embodiment of this invention provides improvements in the production of hydrocarbonaceous middle distillate fuels. Such improvements comprise controlling or reducing the sulfur content of the fuel to a level of 500 ppm or less (preferably 100 ppm or less and most preferably no more than 60 ppm) and blending organic nitrate combustion improver with the resultant reduced sulfur-containing fuel.

Additional embodiments of this invention involve improvements in the operation of motor vehicles and aircraft which operate on middle distillate fuels. These improvements involve fueling the vehicle or aircraft with a hydrocarbonaceous middle distillate fuel characterized by having a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and containing a minor combustion-improving amount of at least one organic nitrate combustion improver dissolved therein.

In accordance with a particularly preferred embodiment of this invention, there is provided a hydrocarbonaceous middle distillate fuel having a sulfur content of not more than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and a 10% boiling point (ASTM D-86) in the range of about 154° to about 230°C, said fuel containing a minor combustion improving amount of at least one fuel-soluble organic nitrate combustion improver. Such fuel compositions tend on combustion to emit especially low levels of NO_x. Without desiring to be bound by theoretical considerations, one explanation for such highly desirable performance is that fuels with higher 10% boiling points cause a delay in the progression of combustion and consequent higher peak temperatures which increase the amount of NO_x formation.

Pursuant to another particularly preferred embodiment of this invention there is provided a hydrocarbonaceous middle distillate fuel having a sulfur content of not more than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and a 90% boiling point (ASTM D-86) in the range of about 260° to about 320°C, said fuel containing a minor combustion improving amount of at least on fuel-solubl organic nitrate combustion improver. Such fuel compositions tend on combustion to emit especially low lev ls of particulates.

These and other embodiments are set forth in the ensuing description and appended claims.

In the accompanying drawings:

Fig. 1 is a l ast-squares plot of NO_x missions versus 10% boiling temperatures of fuels having a nominal cetane number of approximately 50; and

Fig. 2 is a least-squares plot of particulate emissions versus 90% boiling temperatures of fuels having a nominal cetane number of approximately 50.

The hydrocarbonaceous fuels utilized in the practice of this invention are comprised in general of mixtures of hydrocarbons which fall within the distillation range of about 160 to about 370°C. Such fuels are frequently referred to as "middle distillate fuels" since they comprise the fractions which distill after gasoline. Such fuels include diesel fuels, burner fuels, kerosenes, gas oils, jet fuels, and gas turbine engine fuels.

Preferred middle distillate fuels are those characterized by having the following distillation profile:

	°F	°C
IBP	250 - 500	121 - 260
10%	310 - 550	154 - 288
50%	350 - 600	177 - 316
90%	400 - 700	204 - 371
EP	450 - 750	232 - 399

Diesel fuels having a clear cetane number (i.e., a cetane number when devoid of any cetane improver such as an organic nitrate) in the range of 30 to 60 are preferred. Particularly preferred are those in which the clear cetane number is in the range of 40 to 50.

The organic nitrate combustion improvers (also frequently known as ignition improvers) comprise nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to 10 carbon atoms. The alkyl group may be either linear or branched (or a mixture of linear and branched alkyl groups). Specific examples of nitrate compounds suitable for use in the present invention include, but are not limited to, the following: methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentylnitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, isopropylcyclohexyl nitrate, and the like. Also suitable are the nitrate esters of alkoxy substitued aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, 1-methoxypropyl-2-nitrate, and 4-ethoxybutyl nitrate, as well as diol nitrates such as 1,6-hexamethylene dinitrate, and the like. Preferred are the alkyl nitrates having from 5 to 10 carbon atoms, most especially mixtures of primary amyl nitrates, mixtures of primary hexyl nitrates, and octyl nitrates such as 2-ethylhexyl nitrate.

As is well known, nitrate esters are usually prepared by the mixed acid nitration of the appropriate alcohol or diol. Mixtures of nitric and sulfuric acids are generally used for this purpose. Another way of making nitrate esters involves reacting an alkyl or cycloalkyl halide with silver nitrate.

The concentration of nitrate ester in the fuel can be varied within relatively wide limits with the proviso that the amount employed is at least sufficient to cause a reduction in emissions. Generally speaking, the amount employed will fall in the range of about 250 to about 10,000 parts by weight of organic nitrate per million parts by weight of the fuel. Preferred concentrations usually fall within the range of 1,000 to 5,000 parts per million parts of fuel.

Other additives may be included within the fuel compositions of this invention provided they do not adversely affect the exhaust emission reductions achievable by the practice of this invention. Thus use may be made of such components as organic peroxides and hydroperoxides, corrosion inhibitors, antioxidants, antirust agents, detergents and dispersants, friction reducing agents, demulsifiers, dyes, inert dilu nts, and like materials.

The advantages achievable by the practice of this invention were demonstrated in a sequential series of engine tests in which a Detroit Diesel 11.1 liter S ries 60 engine mounted to an engine dynamom ter was used. The system was operated n the "EPA Engine Dynamometer Schedule for Heavy-Duty Diesel Engines" set forth at pages 810-819 of Volume 40, Part 86, Appendix I, of the Code of F deral Regulations (7-1-86). In these tests, th first of five consecutive tests involved operation of the engine on a conv ntional DF-2 diesel fuel hav-

ing a nominal sulfur content in the range of 2000 to 4000 ppm. This test served as on of two baselines. In the next operation the engine was run using a low-sulfur diesel fuel having the following characteristics:

Sulfur, ppm	50
Gravity, API @ 60°F	34.7
Pour Point, °F	-5
Cloud Point, °F	8
Copper Strip	1
Distillation, °F	
IBP	332
10%	430
50%	532
90%	632
EP	634
Cetane Number	44.3
Viscosity @ 40°C, cS	2.96

In the third and fourth tests -- which represented the practice of this invention -- this same low-sulfur fuel was used except that it had blended therein a diesel ignition improver composed of 2-ethylhexyl nitrate. In the third test the concentration was 2000 ppm of the organic nitrate. In the fourth test, the fuel contained 5000 ppm of the organic nitrate. The fifth and final test involved another baseline run using the initial conventional DF-2 diesel fuel. In all instances the quantities of NO_x, unburned hydrocarbons ("HC"), carbon monoxide ("CO") and particulates emitted by the engine were measured and integrated. The results of these tests are summarized in the following table. The values shown therein for NO_x, HC, CO, and Particulates, are presented in terms of grams per brake horsepower per hour. Thus the lower the value, the lower the rate and amount of emissions.

Test No.	NOx	HC	CO	Particulates
1	4.641	0.086	1.414	0.227
2	4.345	0.068	1.490	0.165
3	4.173	0.051	1.312	0.164
4	4.208	0.073	1 324	0.165
5	4.623	0.078	1.525	0.223

In particularly preferred embodiments of this invention, use of fuels having certain boiling characteristics as well as low sulfur levels, results in still further reductions in either NO_x or particulate emissions. Thus by use of fuels meeting the low sulfur parameters set forth hereinabove and additionally having a 10% boiling point (ASTM D-86) in the range of 154-230°C, the emissions of NO_x can be reduced to extremely low levels. Likewise, by use of fuels meeting the low sulfur parameters set forth hereinabove and additionally having a 90% boiling point (ASTM D-86) in the range of 260-320°C, particulate emissions tend to be reduced to especially low levels. To illustrate, a Detroit Diesel Corporation Series 60 Engine in the 11.1 liter configuration and nominally rated at 320 hp at 1800 rpm was used in a series of emission tests. The engine was installed in a heavy-duty transient emission c ll equipped with a constant volum sampl r (CVS) system. A dilution tunnel permitted measurements of HC, CO, NO_x and particulates according to the EPA Transient Emissions Cycle Procedure.

For ach individual t st case, th engin was started and warmed up. It was then run f r 20 minutes at rated speed and load. Rated power was validated. In addition, a pow r test was conducted, mapping ngine

torque vs. speed. These parameters are required as part of the EPA Transient Cycl Procedure. Once this information was obtained, two 20-minut EPA Transient Cycles were run and engine controls were adjusted to meet statistical operating limits prescribed for the tests. The engine was shut down and allowed to soak for 20 minutes. At the end of the soak period, the Hot Start EPA Transient Cycle was run to measure NO_x, CO and particulate emissions. A second emissions evaluation was conducted after another two-minute soak. Results for the two Hot Transient Cycles were averaged into a final reported value. Whenever a fuel was changed, new fuel was introduced into the fueling system, new fuel filters were installed, and fuel lines were flushed.

Each fuel (A through D) was evaluated by the same Hot Start EPA Transient Emissions Cycle Procedure. Fuels A, B, and C contained 2-ethylhexyl nitrate in an amount sufficient to raise the cetane number of the respective fuels to a nominal value of 50. Fuel D which had a natural cetane number of 49.8 was used unadditized.

Physical and chemical characterization data for unadditized fuels A through D are shown in the following table:

TABLE

Fuel Property	A	B	C	D
Hydrocarbon Composition, vol %				
Aromatics	36.5	28.5	37.6	39.4
Olefins	1.2	1.1	2.2	2.9
Saturates	62.3	70.4	60.2	57.7
Carbon, wt%	86.35	86.49	86.12	87.32
Hydrogen, wt%	13.15	13.25	12.89	13.35
Nitrogen, ppm	5.3	285	356	152
Sulfur, ppm	<1	225	219	476
Aniline pt., deg. C	70.1	60.0	65.4	69.4
Diene content, wt%	<0.1	0.2	<0.1	<0.1
Viscosity, cSt				
@ 40 deg. C	2.99	2.20	3.10	3.53
@ 100 deg. C	1.22	0.97	1.23	1.34
Heat of combustion BTU/lb	19,593	19,840	19,543	19,672
Boiling range, deg. C				
IBP	170	172	202	218
10%	217	211	234	252
20%	233	222	246	262
30%	249	230	257	271
40%	262	237	267	278
50%	274	244	276	284
60%	288	253	286	291
70%	300	263	294	298
80%	314	276	306	306
90%	331	297	322	317
95%	344	319	338	329
FBP	352	334	353	341
Recovery, %	98.7	98.9	98.6	98.9
Gravity, deg. API	34.9	36.1	34.6	34.5
Specific gravity	0.850	0.844	0.852	0.852
Calculated cetane index	48.1	44.0	48.9	51.7
Cetane index	48.5	43.8	48.3	49.7
Cetane number	45.3	39.6	47.7	49.8

In the above table, the following test methods were used:

Hydrocarbon composition - ASTM D-1319
Carbon - Carlo-Erba 1106
Hydrogen - Carlo-Erba 1106
Nitrogen - ASTM D-4629
Sulfur - ASTM D-3120
Aniline pt. - ASTM D-611
Diene content - UOP 326
Viscosity - ASTM D-445

Heat of combustion - ASTM D-2382
Boiling range - ASTM D-86
Gravity - ASTM D-287
Calculated cetane index - ASTM D-4737
Cetane index - ASTM D-976
Cetane number - ASTM D 613

Fig. 1 presents graphically the results of NO_x emissions in relation to the 10% boiling temperatures of the four fuels. It can be seen that the fuels in which the 10% boiling temperature was below 230°C had the lowest NO_x emissions.

The results of the particulate determinations are graphically depicted in Fig. 2. In this case, the results are shown as a function of 90% boiling temperatures of the base fuels. A trend toward lower particulate emissions with fuels having 90% boiling points within the range of 260-320°C was noted.

Methods for reducing the sulfur content of hydrocarbonaceous middle distillate fuels or their precursors are reported in the literature and are otherwise available to those skilled in the art. Among such processes are solvent extraction using such agents as sulfur dioxide or furfural, sulfuric acid treatment, and hydrodesulfurization processes. Of these, hydrodesulfurization is generally preferred, and includes a number of specific methods and operating conditions as applied to various feedstocks. For example, hydrotreating or hydroprocessing of naphthas or gas oils is generally conducted under mild or moderate severity conditions. On the other hand, sulfur removal by hydrocracking as applied to distillate stocks is usually conducted under more severe operating conditions. Vacuum distillation of bottoms from atmospheric distillations is still another method for controlling or reducing sulfur content of hydrocarbon stocks used in the production of hydrocarbonaceous middle distillate fuels. Further information concerning such processes appears in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Interscience Publishers, Volume 11, pages 432-445 (copyright 1966) and references cited therein; Idem., Volume 15, pages 1-77 and references cited therein; and Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 17, Third Edition, Wiley-Interscience, pages 183-256 (copyright 1982) and references cited therein. All of such publications and cited references are incorporated herein by reference in respect of processes or methods for control of reduction of sulfur content in hydrocarbonaceous middle disillate fuels or their precursor stocks.

Another method which can be used involves treatment of the hydrocarbonaceous middle distillate fuel with a metallic desulfurization agent such as metallic sodium, or mixtures of sodium and calcium metals.

Other similar embodiments of this invention will readily occur to those skilled in the art from a consideration of the foregoing disclosure.

Claims

1. A fuel composition comprising a major proportion of a hydrocarbonaceous middle distillate fuel which has a sulfur content of less than 500 ppm and a minor combustion-improving amount of at least one organic nitrate combustion improver dissolved therein.

2. The composition of claim 1 wherein the base fuel has a 10% boiling point (ASTM D-86) in the range of 154-230°C.

3. The composition of claim 1 or 2 wherein the base fuel has a 90% boiling point (ASTM D-86) in the range of 260-320°C.

4. The composition of any of claims 1-3 wherein the base fuel has a sulfur content of 100 ppm or less and a clear cetane number in the range of 30-60.

5. The composition of any of claims 1-3 wherein the base fuel is a diesel fuel having a clear cetane number in the range of 30-60.

6. The composition of any of the preceding claims wherein the organic nitrate combustion improver consists ssentially of a nitrate ester of at least one primary alkanol having 5-10 carbon atoms in the molecule.

7. The use, in combustion process wherein a middle distillate fuel is subjected to combustion in th presence of air, of a hydrocarbonaceous middl distillate fuel having a sulfur content of less than 500 ppm and having dissolved therein a minor combustion-improving amount of at least one organic nitrate combustion

improver.

8. A process for the production of a hydrocarbonaceous middle distillate fuel, in which the sulfur content of the fuel is controlled to a level of 500 ppm or less and at least one organic nitrate combustion improver is blended with the resultant reduced sulfur-containing fuel.

9. The use, in the operation of a motor vehicle which operates on middle distillate fuel, of a hydrocarbonaceous middle distillate fuel for said vehicle having a sulfur content of less than 500 ppm and containing a minor combustion-improving amount of at least one organic nitrate combustion improver dissolved therein.

10. The use, in the operation of an aircraft which operates on middle distillate fuel, of a hydrocarbonaceous middle distillate fuel for said aircraft having a sulfur content of less than 500 ppm and containing a minor combustion-improving amount of at least one organic nitrate combustion improver dissolved therein.

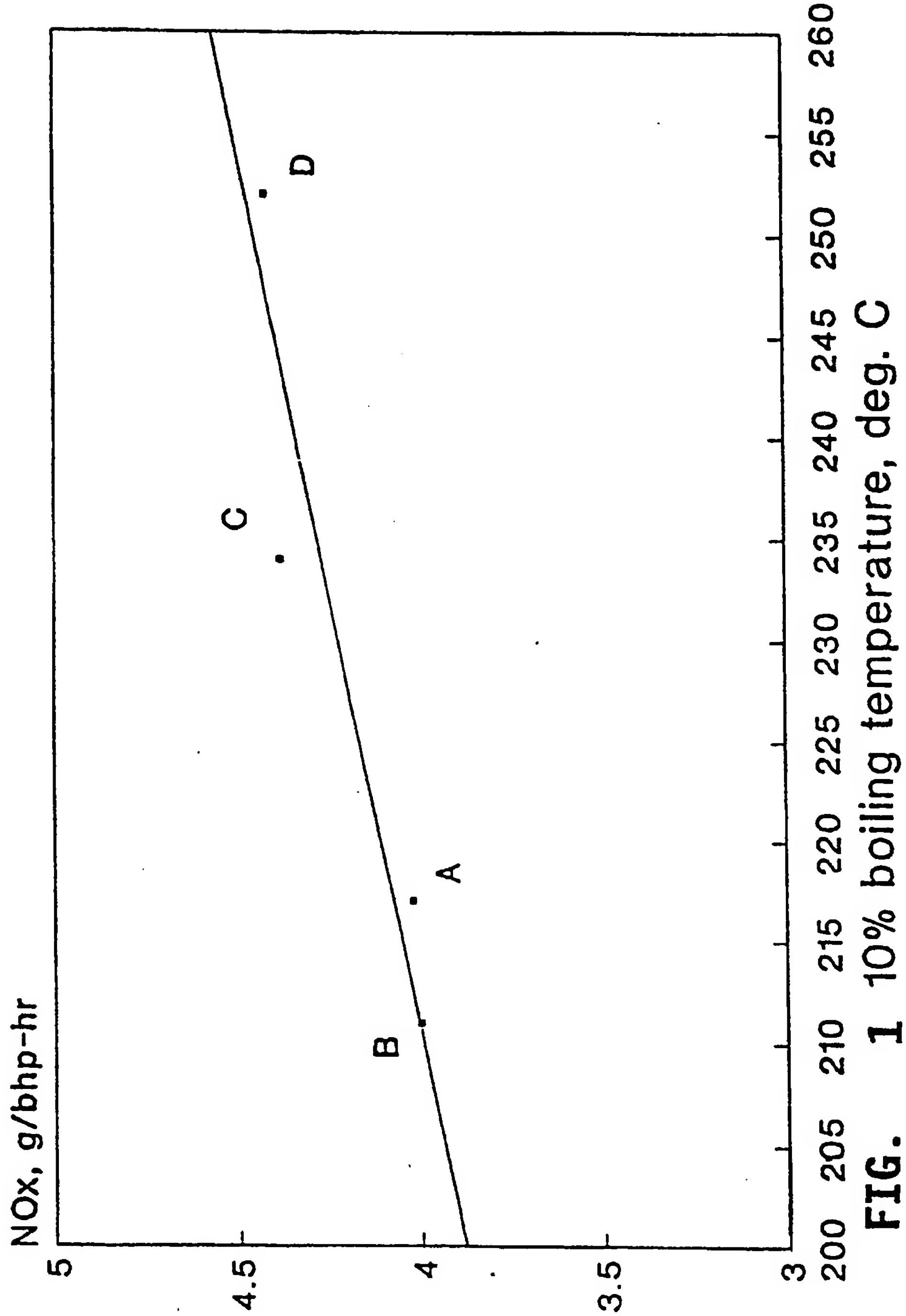
NOx, g/bhp-hr
5
4.5
4
3.5
3
200
205
210
215
220
225
230
235
240
245
250
255
260
A
B
C
D
10% boiling temperature, deg. C

FIG. 1

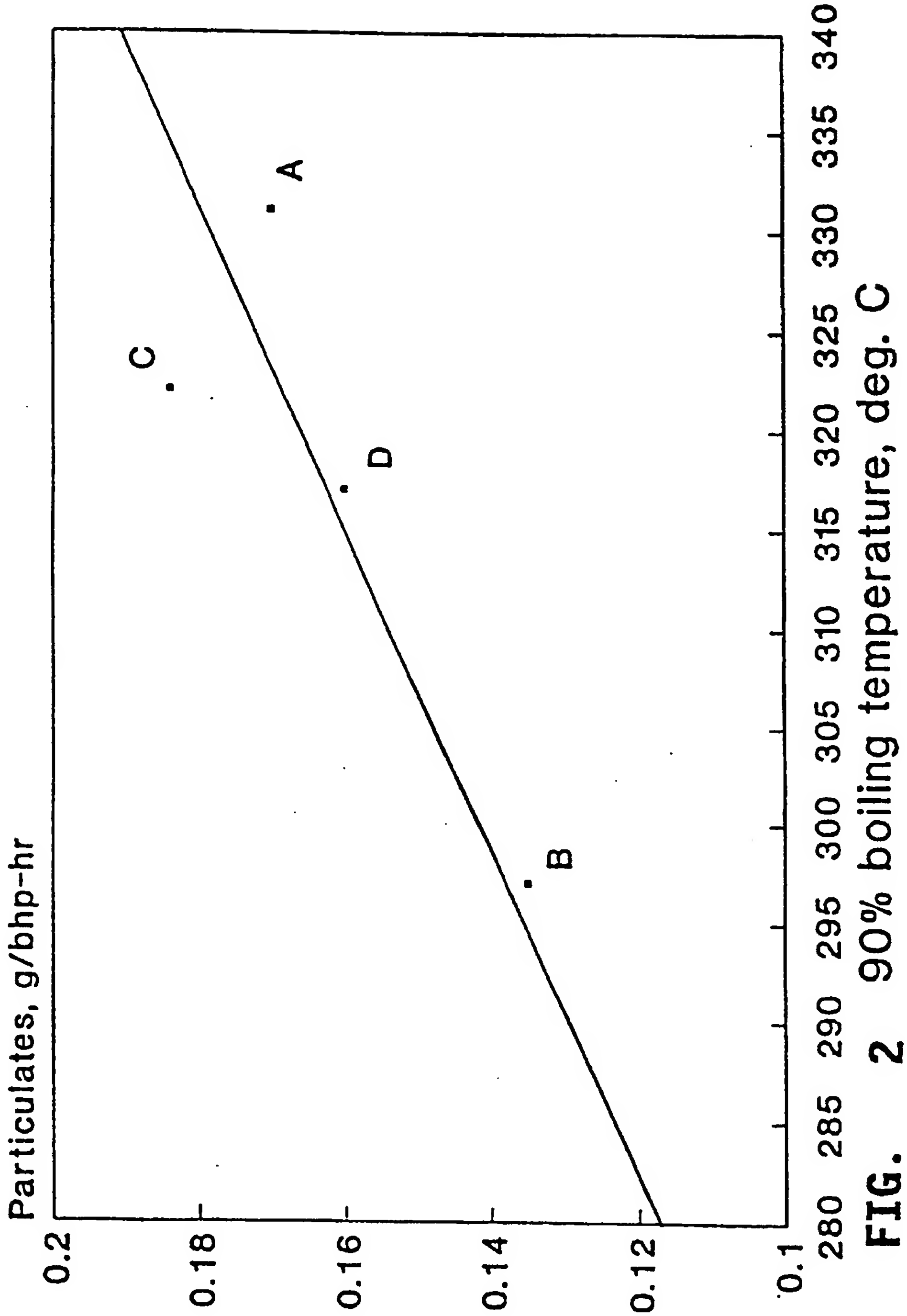
Particulates, g/bhp-hr
0.2
0.18
0.16
0.14
0.12
0.1
280
285
290
295
300
305
310
315
320
325
330
335
340
A
B
C
D
90% boiling temperature, deg. C

FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 4405

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DE-A-3 233 834 (RUHRCHEMIE AG) * the whole document *	1-9	C 10 L 1/22
Y	GB-A-1 547 664 (EXXON) * the whole document *	1-10	
Y	US-A-4 448 587 (HINKAMP ET AL.) * the whole document *	1-9	
Y	US-A-4 073 626 (SIMMONS) * the whole document *	1,7-9	
Y	US-A-2 031 497 (MARVEL) * the whole document *	1,6-9	
Y	FR-A-1 349 941 (ESSO) * the whole document *	1,6-8	
Y	US-A-4 561 862 (DORY) * the whole document *	1-5,7-9	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	GB-A- 697 730 (C. W. HODGSON) * the whole document *	1,7-10	C 10 L C 10 G
A	US-A-4 328 005 (FRANKEL ET AL) * the whole document *	1-10	
X	FR-A- 821 211 (BERESLAVSKY) * see pages 5,6 *	1-9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-08-1991	DE LA MORINERIE B.M.S.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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